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2-Iodoxybenzoic acid ditriflate: the most powerful hypervalent iodine(V) oxidant†

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A ditriflate derivative of 2-iodoxybenzoic acid (IBX) was prepared by the reaction of IBX with trifluoromethanesulfonic acid and characterized by single crystal X-ray crystallography. IBX-ditriflate is the most powerful oxidant in a series of structurally similar IBX derivatives which is best illustrated by its ability to readily oxidize hydrocarbons and the oxidation resistant polyfluoroalcohols.

In recent years, interest in synthetic applications of hypervalent iodine compounds as versatile oxidizing reagents and catalysts has undergone explosive growth.[1–9] Hypervalent iodine(V) reagents represent a particularly important class of oxidants extensively employed in organic synthesis. 2-Iodoxybenzoic acid (IBX, structure **1** in Fig. 1) and the product of its acetylation Dess–Martin periodinane (DMP, **2**) have become the most common oxidizing reagents used for the selective oxidation of alcohols to carbonyl compounds and other synthetically useful oxidative transformations.[10,11] However, IBX and DMP are mild oxidants with a relatively low reactivity, which significantly limits their synthetic applications. In the search for the more powerful iodine(V) oxidants, several IBX derivatives have been synthesized and investigated.[12–16] The most notable powerful iodine(V) oxidants are represented by the highly electrophilic IBX-tosylate and IBX-OTs diacetate **3**,[16] which show high reactivity in the oxidation of structurally complex primary and secondary alcohols.[17] In the present communication, we report the preparation, structure and reactivity of IBX-ditriflate **4**, the most powerful oxidant in the series of structurally similar IBX derivatives (Fig. 1).

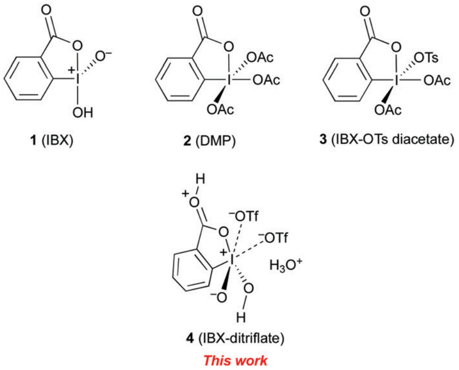
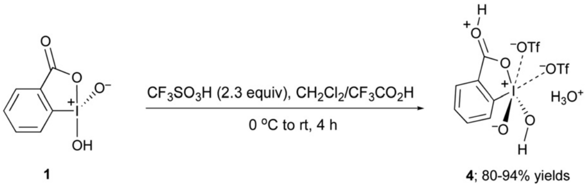


Fig. 1 Structures of IBX, DMP and their tosylate and ditriflate derivatives.

We have prepared IBX-ditriflate **4** by the reaction of IBX **1** with trifluoromethanesulfonic acid (2 equiv.) in dichloromethane in the presence of trifluoroacetic acid (Scheme 1). Product **4** was isolated in the form of a moderately hygroscopic, white, microcrystalline precipitate that can be separated by filtration directly from the reaction mixture. Triflate **4** can be stored for several months at room temperature; it melts with gradual decomposition at 110–112 °C, and it does not demonstrate any explosive properties. We have prepared compound **4** in multigram quantities numerous times with yields ranging from 80 to 94%. According to elemental analysis, a sample of product **4** prepared by recrystallization in open air is a complex of IBX with two molecules of trifluoromethanesulfonic acid. The ^{1}H NMR spectrum of triflate **4** displayed signals in the aromatic region corresponding to the benziodoxole unit, while ^{13}C NMR



Scheme 1 Preparation of IBX-ditriflate **4**.

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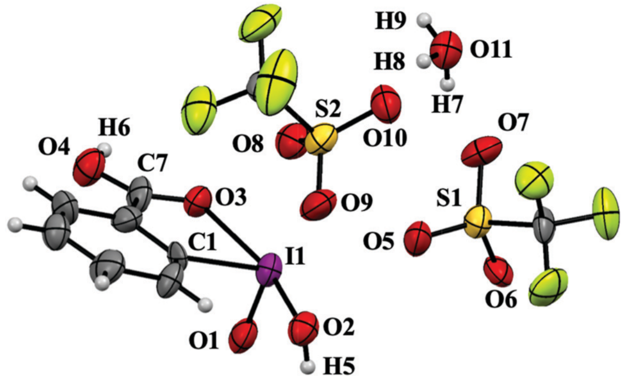


Fig. 2 ORTEP drawing of the X-ray crystal structure of compound **4** at 50% ellipsoid probabilities.

displayed the signal of C–I(v) at about 147 ppm, which is typical of organoiodine(v) derivatives.

X-ray crystallographic study of a single crystal of **4** revealed a complex structure characterized by numerous intramolecular and intermolecular secondary contacts in the solid state (Fig. 2 and 3).‡ Chemical formula **4** shown in Scheme 1 provides a simplified structural presentation of the crystal structure illustrated by the ORTEP drawing in Fig. 2. The selected bond distances and angles for compound **4** are listed in Table 1. The iodine(v) center has a pseudo pentagonal bipyramidal coordination sphere formed by four short intramolecular bonds between I1–C1, I1–O1, I1–O2, and I1–O3 and three longer contacts with two neighboring triflate anions (I1–O5 and I1–O9) and an oxygen atom of the neighboring iodine(v) molecule (I1–O1(A)). The distances between the iodine center and the triflate anions (2.820 Å and 2.985 Å) are within a typical range of iodonium triflate salts.[7] The axial I1–O1 bond is short and has double bond character, while the equatorial I1–O2 bond is within a typical range for I–OH single bonds. The I1–C1 bond in **4** is in a typical range for iodine(v) compounds. Long-range order in the crystal structure of **4** is driven by the extended networks of hydrogen bonds (Fig. 3). First, the hypervalent iodine(v) molecules ordered by an infinite polymeric chain formed by the short I1═O1···H5(A)–O2(A)–I1(A) hydrogen bond. In addition, a second chain of hydrogen bonds is formed between the protonated carboxylic acid group of the iodine(v) molecule and an oxygen atom of one of the triflate anions (C7–O4–H6···O6(A) contact). Finally, triflate anions are connected by three hydrogen bonds provided by the hydronium cation (H7···O7, H8···O10, and H9···O8).

Table 1 Selected bond distances in the molecule of **4**

Bond	Distance [Å]	Bond	Distance [Å]
I_1–O_1	1.790(12)	C_7–O_3	1.248(16)
I_1–O_2	1.881(10)	C_7–O_4	1.288(18)
I_1–O_3	2.377(10)	$I_1\cdots O_9$	2.820(18)
I_1–C_1	2.102(11)	$I_1\cdots O_5$	2.985(16)
$H_6\cdots O_6$	1.797	$I_1\cdots O_1$(A)	2.897(17)
$O_1\cdots H_5$(A)	1.897	$H_8\cdots O_{10}$	1.776
$H_7\cdots O_7$	1.795	$H_9\cdots O_8$	1.854

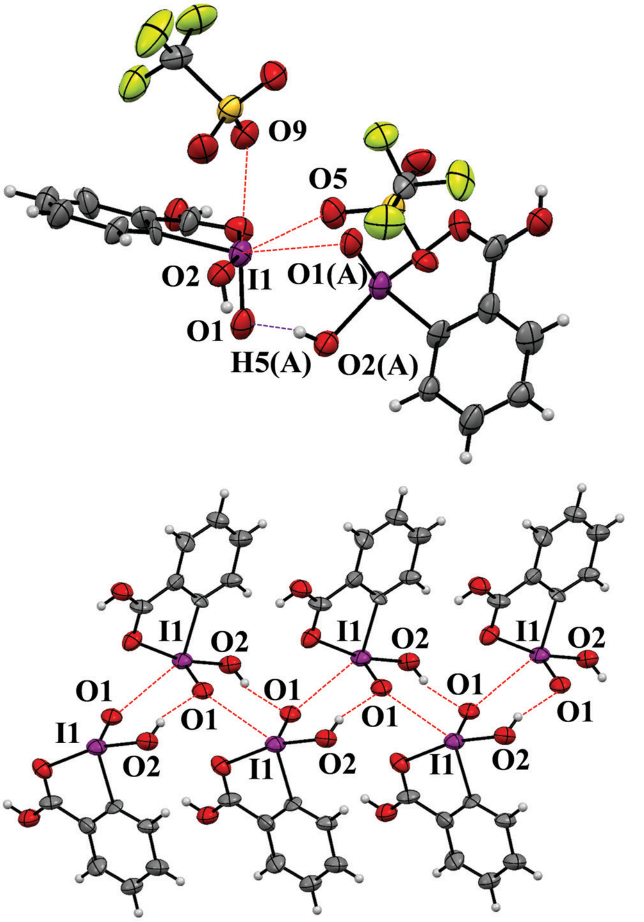
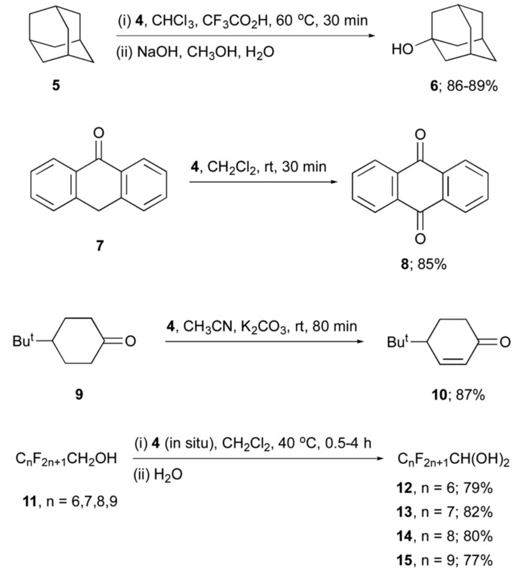


Fig. 3 Secondary interactions found in the crystal structure of **4** (at the 50% probability level).

IBX-ditriflate is an extremely active oxidant towards most organic compounds. It oxidizes common organic solvents such as hexane or ether in a few minutes forming a complex mixture of products. Solutions of compound **4** in acetonitrile are stable for 1–2 hours and then the ^{13}C NMR signal of C–I(v) at about 147 ppm gradually disappears. According to a mass-spectrometry study (see ESI,† p. S15), after 3 hours in acetonitrile IBX-ditriflate is completely converted to the corresponding iodine(III) derivative, pseudocyclic benziodoxole triflate.[18] Only solutions of triflate **4** in trifluoroacetic acid or in chlorinated solvents such as chloroform and dichloromethane are relatively stable.

Most of the common organic compounds are non-selectively oxidized by IBX-ditriflate producing black tar. However, we were able to perform several selective oxidations of generally non-reactive organic substrates using compound **4** in pure form or generated *in situ* from IBX and triflic acid (Scheme 2). In particular, adamantane **5** is quickly oxidized by a solution of reagent **4** in trifluoroacetic acid to produce 1-adamantanol **6** in high isolated yield. Previously known procedures for direct oxidation of adamantane to adamantanol in a very low yield (1–5%) utilized oxo ruthenium complexes[19] or hypervalent iodine reagents in the presence of iron(III) phthalocyanine complexes as catalysts.[20] The oxidation of adamantane to 1-adamantanol in similar yields



Scheme 2 Oxidation of organic substrates with IBX-ditriflate **4**.

can also be performed with IBX-ditriflate generated *in situ* from IBX and triflic acid in trifluoroacetic acid. The oxidation of anthracen-9(10*H*)-one **7** with reagent **4** proceeds at room temperature in 30 min to afford anthraquinone **8** as a single product. The reaction of 4-(*tert*-butyl)-cyclohexanone **9** with IBX-ditriflate in acetonitrile at room temperature results in oxidative dehydrogenation leading to an α,β-unsaturated carbonyl product **10**. Similar oxidative dehydrogenation reactions of carbonyl compounds using IBX in DMSO proceed at 65–85 °C and require 24–48 hours for completion,[21] which is indicative of a significantly higher reactivity of IBX-ditriflate compared to IBX.

The excellent oxidizing properties of reagent **4** towards alcohols are best illustrated by its ability to oxidize polyfluorinated alcohols, which show an outstanding resistance to various oxidants and are commonly used as solvents for oxidations with hypervalent iodine reagents.[22] Using ^{1}H NMR monitoring, we have found that reagent **4** readily oxidizes 2,2,2-trifluoroethanol (TFE) in $CDCl_3$ to the respective aldehyde (in the form of acetals and hemiacetals) in almost 100% conversion after 2 hours (see ESI† for details). Under identical conditions, no oxidation of TFE occurs with IBX. 1,1,1,3,3,3-Hexafluoroisopropanol (HFIP) is oxidized with 99% conversion at 60 °C in just 30 min. For comparison, the oxidation of HFIP with IBX-tosylate at 60 °C proceeds with only 60% conversion after 7 hours.[16] The oxidation of higher polyfluorinated alcohols **11** can be conveniently performed using IBX-ditriflate generated *in situ* from IBX and triflic acid in dichloromethane. Polyfluoroaldehydes resulting from these oxidations were isolated after aqueous work-up in the form of *gem*-diols **12–15** in high yields (Scheme 2). It should be emphasized that previously known procedures for the preparation of polyfluoroaldehydes (in the form of *gem*-diols) are based on the reduction of corresponding polyfluorocarboxylic acids or other indirect methods.[23–29] Polyfluoroaldehydes represent a practically important class of organofluorine compounds;[30] however, to the best of our knowledge, their preparation by the direct oxidation of readily available polyfluorinated primary alcohols was not previously reported in the literature.

In conclusion, we have reported the preparation of a new powerful hypervalent iodine(V) oxidant, a ditriflate derivative of 2-iodoxybenzoic acid (IBX-ditriflate **4**), by the reaction of IBX with triflic acid. Single crystal X-ray crystallography of IBX-ditriflate **4** revealed an unusual heptacoordinated iodine geometry with significant intermolecular secondary interactions. According to the X-ray data, the I–OTf bond in compound **4** has a significant ionic character, which leads to the high electrophilic reactivity of this compound in oxidation reactions. Pentavalent iodine triflate **4** can be used as an efficient oxidizing reagent toward a variety of generally nonreactive organic substrates including polyfluorinated primary alcohols.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ Crystal data for **4** $C_9H_9F_6I_1O_{11}S_2$: M 598.19, monoclinic, space group $P21/n$, a = 15.4493(5), b = 5.7324(2), c = 20.1514(14) Å, β = 97.086(7)°, V = 1771.01(12) Å^3, Z = 4, μ = 17.569 mm^{-1}, 8356 reflections measured, 2811 unique; final R_1 = 0.0953, R_w = 0.2256. CCDC 1908422.†

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